

# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### Method of producing Hard, Abrasion-Resistant Coatings on Aluminum and Aluminum Alloys

We, THE GLENN L. MARTIN COMPANY, a Corporation organized and existing under the laws of the State of Maryland, United States of America, of Middle River, Baltimore County, Maryland, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of hard, abrasion-resistant coatings on aluminum (synonymous with aluminium) and aluminum alloys, and more particularly to a method for the production of such coatings on aluminum and aluminum alloys by anodic oxidation in large scale operations under conditions such that "burning" or spoilage of the work pieces is avoided.

Thus, a principal object of the present invention is to provide a new and improved method for producing by anodic oxidation upon aluminum and aluminum alloys coatings that are characterized by a high degree of hardness, abrasion resistance and corrosion resistance, wherein the method affords substantial freedom from "burning" or spoilage of the work pieces during large scale coating operations.

The manner in which these and other objects and features of the invention are attained will appear more fully from the following description thereof, in which reference is made to typical and preferred procedures in order to indicate more fully the nature of the invention, but without intending in any way to limit the scope of the invention thereby.

The process of the present invention is an improvement upon that described and claimed in our prior copending application No. 1522/51 (Serial No. 701,390), the disclosure of which therefore is to be regarded, for the sake of brevity, as incorporated herein by reference.

In that prior application reference was [Price 2/8]

made to the then-previous state of the art relating to the anodic oxidation of aluminum and aluminum alloys in suitable electrolytes such as aqueous sulphuric acid and the like, such as is represented, for example, by Bengston, U.S. Patents Nos. 1,869,041, 1,869,042, and 1,891,703, Tosterud, U.S. Patent No. 1,900,472, and Work U.S. Patent No. 1,965,682. According to such methods, the aluminum or aluminum alloy article to be coated is made the anode in an electrolytic cell having a lead cathode and an electrolyte comprising aqueous sulphuric acid, and the desired coating is produced upon the article by passing a direct current having suitable voltage and current density characteristics through the system, all in a manner generally well known to those skilled in the art. The coatings that result are comprised principally of aluminum oxide and possess varying degrees of abrasion resistance.

In accordance with the process described and claimed in our prior copending application, we had discovered that coatings of substantially greater thickness and much higher abrasion resistance could be produced on aluminum and aluminum alloy articles if the prior art coating conditions were modified by subjecting the articles to anodic oxidation while in contact with an aqueous coating forming electrolyte, the electrolyte being maintained at a temperature below 40° F. during the entire coating operation. Coatings that were much thicker and more highly abrasion-resistant than those theretofore known in the art were produced in that manner. Expressed somewhat differently, it was found that those results were obtained if the electrolyte temperature was maintained at not more than 40° F., and preferably not more than approximately 35° F., electrolyte temperatures of about 30° F. representing particularly satisfactory operating conditions.

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While the process described and claimed in our prior copending application operates very satisfactorily and with uniformly good results on a relatively small scale, when attempting to translate the process into large scale operation with large scale electrolyte plating tanks of large capacity, for example of the order of 400 gallons, it was found that operating difficulties were sometimes encountered, particularly when operating upon work pieces having at least one short dimension, such as sheets and other parts having thin sections. Under these circumstances it was found that work pieces, such as sheets of aluminum and aluminum alloys, were sometimes deleteriously affected during the coating operation. For example, it was found that under such circumstances thin sheets of aluminum approximately six inches square were sometimes as much as one-half consumed in an effort to coat them in plant scale operations. The reason for this phenomenon, which we herein refer to as "burning" is not known, but obviously the sometimes erratic behaviour of the coating operation when conducted on a large plant scale could not be tolerated.

According to the present invention, we have now discovered that difficulties of the nature referred to above are completely eliminated when carrying out on a large plant scale the process described and claimed in my prior copending application if the process is conducted in the presence of  $\text{CO}_2$  in the electrolytic bath. The  $\text{CO}_2$  may be introduced in the form of "dry ice" which is simply thrown into the electrolytic bath in the plating tank, preferably in sufficient quantities to insure that the electrolytic bath will be saturated or substantially saturated with  $\text{CO}_2$ . Alternatively the  $\text{CO}_2$  may be introduced by simply bubbling  $\text{CO}_2$  gas from a suitable storage container through a nozzle or series of nozzles disposed along the sides and/or bottom of the plating tank, preferably at a rate such as to insure an excess of  $\text{CO}_2$ . The electrolytic bath in the tank is preferably subjected to agitation by a suitable mechanical stirring device, although in some cases the introduction of the  $\text{CO}_2$  gas under pressure from a series of orifices strategically located throughout the tank will provide sufficient agitation. Suitable agitation may also result from circulating the electrolyte continuously between the tank and an outside cooler of sufficient refrigerating capacity to maintain the temperature of the electrolyte in the tank within the limits described above throughout the entire coating operation.

The actual anodizing operation may be carried out under a wide variety of conditions so long as the temperature is maintained as described above, and so long as the operation is conducted in the presence of  $\text{CO}_2$ . Some of these process variables which *per se* are known to the art and which therefore do not in and of themselves constitute the present invention may be briefly mentioned as follows:—

The electrolyte may be an aqueous solution of sulphuric acid in which the acid concentration varies from about 5 to 70%  $\text{H}_2\text{SO}_4$ . Acid concentrations of from 5 to 25% are particularly satisfactory, with about 15%  $\text{H}_2\text{SO}_4$  representing an optimum value for many coating operations.

Conventional coating bath additives may be present in the electrolyte, such as oxalic and other organic acids (see Work, U.S. Patent No. 1,965,682), glycerin, and the like.

Current densities varying from about 10 to 50 amperes per square foot, and preferably from about 20 to 25 amperes per square foot, may be employed.

The voltage may vary from about 25 to 30 volts at the start of the operation, gradually increasing during the course of the operation to a maximum of the order of 40 to 100 volts. The current density may be suitably regulated by gradually increasing the voltage during the course of the coating operation so as to maintain the desired current density.

Either direct current or alternating current may be employed, although the former is preferred.

The coating times may vary over rather wide ranges, although from  $\frac{1}{2}$  to 4 hours is satisfactory for most purposes. A particularly desirable coating time is approximately 90 minutes when operating at current densities of approximately 20–25 amperes per square foot in which case the thickness of the anodic film produced thereby is of the order of approximately 0.002 inches.

No after-treatment of the coating is required except a plain water rinse in order to remove residual electrolyte from the surface of the work piece. No pre-treatment of the work piece is necessary except of course the conventional one of first treating the articles to be coated, if necessary, with a suitable cleansing bath in order to make sure that they are clean and free from grease and dirt or dust. The finished coatings may be dyed by standard dyeing techniques well known in this particular art, and in this manner may be coloured black, blue, red, yellow, etc., as desired.

If desired the coating may be "sealed" 130

by dipping it in hot water maintained at a temperature from about 160° F. to the boiling point for a period of about 10 minutes, which apparently has the effect of changing the coating from an amorphous aluminum oxide to the monohydrate form. It should be noted, however, that this treatment imparts maximum corrosion resistance to the coating but at the expense of its abrasion resistance, and hence it is not recommended under circumstances where maximum abrasion resistance is required.

The coatings obtained by this process are coloured from light gray to nearly black, depending in part at least upon the particular aluminum or aluminum alloy composition undergoing treatment.

The coatings vary in thickness depending upon the conditions under which they are produced, and especially in accordance with the coating times. Thus the coatings may vary in thickness from 0.00134 inches at a coating time of 60 minutes to 0.0060 inches at a coating time of 240 minutes, when employing preferred conditions of current density (20—25 amperes per square foot) and electrolyte temperature (30° F.).

The coatings may be applied to articles formed of pure or substantially pure aluminum or to articles formed of aluminum alloys in which aluminum is the predominant constituent. Such alloys are generally characterized by an aluminum content of at least approximately 85%, although it should be noted that copper, if present, should not be present to the extent of more than about 5%. Examples of specific aluminum alloys which, aside from pure or substantially pure aluminum, may be coated in accordance with the present invention are as follows:—

"14S" alloy, having a composition of about 4.4% copper, 0.8% silicon, 0.8% manganese, 0.4% magnesium, balance aluminum;

"24S" alloy, having a composition of about 4.5% copper, 1.5% magnesium, 0.6% manganese, balance aluminum;

"61S" alloy, having a composition of about 1% magnesium, 0.6% silicon, 0.25% copper, 0.25% chromium, balance aluminum;

"75S" alloy, having a composition of about 5.5% zinc, 2.5% magnesium, 1.5% copper, 0.3% chromium, 0.2% manganese, balance aluminum.

As described in our prior copending application, the present process is well adapted for use in the large scale coating of aluminum and aluminum alloy parts having certain specialized functions where a thick abrasion-resistant coating is essential. These uses may be said to

fall into three main categories, as follows:—

(1) the treatment of aluminum and aluminum alloy parts intended for use in place of steel parts as a weight-saving measure;

(2) the replacement of aluminum-coated parts in environments where ordinary aluminum parts, either uncoated or coated by methods of the prior art in which conventional coating bath temperatures substantially higher than 40° F. prevail, wear out so rapidly as to render their use economically unfeasible; and

(3) so-called "non-seizure applications" where two or more aluminum parts that normally are employed in relatively tightly co-operative relation with each other tend to seize or freeze upon each other during use, with resultant jamming of the mechanism of which they are a part.

Specific examples of applications of aluminum or aluminum alloy parts or articles coated according to the present invention, and tending to fall in one or more of the three main classes mentioned above, are threaded aluminum parts; bearing surfaces, both sliding and rolling, and including wear plates, swivel joints and friction locks; gears, and particularly the load-carrying tooth portions thereof; prosthetic devices, with particular reference to the load-carrying joints of artificial leg braces in this class of devices; rotor blades, and especially the leading edges of helicopter blades the tips of which frequently travel at supersonic speeds; ball-bearing raceways; intricate structural shapes including tubular shapes in which difficulties normally are encountered in obtaining the necessary throwing power during the coating operation; and aeronautical uses in general where weight-saving combined with a relatively high degree of abrasion resistance are desiderata. The present process is particularly adapted to the treatment of parts or articles of the foregoing nature, or otherwise, having at least one short dimension, and which are to be coated simultaneously in large scale operations.

Aluminum and aluminum alloy articles coated in accordance with the present invention are relatively good heat insulators and also offer excellent resistance to atmospheric and salt spray corrosion. They are also non-conductors of electricity.

In certain applications involving aluminum or aluminum alloy parts coated in accordance herewith, and particularly where relatively heavy bearing pressures

are involved, it is possible further to enhance resistance to sliding wear of the parts so coated by employing them in conjunction with a suitable lubricant material, examples of which are water, graphite, greases, and molybdenum disulfide.

In order to indicate still more fully the nature of the present invention, the following examples of typical procedure are set forth, it being understood that these examples are presented for illustrative purposes only and not as limiting the scope of the invention:—

#### 15 EXAMPLE I

A large number of sheets of "75S" aluminum alloy were coated by anodic oxidation in a large industrial installation having an electrolytic bath capacity of some 400 gallons under the following coating conditions:—

Direct current at a current density of about 20 amperes per square foot.

Voltage at the beginning of the coating operation of approximately 26 volts, and gradually increasing thereafter to maintain the desired current density.

90 minutes coating time.

15%  $H_2SO_4$  electrolyte maintained at 30° F. by circulating the electrolyte through an external mechanical system, with agitation in the plating refrigerating tank maintained throughout the entire coating operation.

Chunks of "dry ice" immersed in the tank in a quantity such that at all times during the entire coating operation there was excess of solid  $CO_2$  present in the bath.

The sheets of aluminum alloy coated in this manner were given a highly abrasion-resistant coating 0.002 inches in thickness. No "burning" of the aluminum alloy sheets was encountered despite the fact that the sheets were coated in a large scale industrial operation under conditions such that, without the presence of the  $CO_2$ , "burning" or consumption of a portion of the aluminum frequently took place.

#### EXAMPLE II

The procedure of the previous example was repeated, but in this instance instead of immersing pieces of "dry ice" in the plating bath during the course of the coating operation,  $CO_2$  gas was bubbled into the agitated electrolytic bath during the entire coating operation by introducing same from a source of supply of the gas under pressure through a coil of pipe provided with a series of perforations and disposed along the bottom of the plating tank.

Similar results were obtained in res-

pect of the uniformly high quality of the resulting coating and freedom from "burning" during the coating operation.

While various specific examples of preferred procedure embodying the above invention have been described above, it will be apparent that many changes and modifications may be made in those methods of procedure without departing from the scope of the invention as set forth in the claims. It should, therefore, be understood that the examples cited and the methods of procedure set forth above are intended to be illustrative only and are not intended to limit the scope of the invention.

What we claim is:—

1. A method of forming a hard, abrasion-resistant coating on a predominantly aluminum surface by subjecting it to anodic oxidation while in contact with an aqueous coating forming electrolyte maintained at a temperature below 40° F. and in the presence of  $CO_2$ .

2. A method for producing a hard, abrasion-resistant coating on the surface of a predominantly aluminum or aluminum alloy article, which method comprises making the article to be coated an anode in an electrolytic cell having an electrolyte comprising an aqueous solution of sulphuric acid, maintaining the electrolyte at a temperature below 40° F. during the entire coating operation, and contacting the electrolyte with  $CO_2$  during the entire coating operation.

3. A method according to claim 1 or 2, wherein the electrolyte is saturated with the  $CO_2$ .

4. A method according to any one of the preceding claims, wherein  $CO_2$  gas is bubbled through the body of the electrolyte.

5. A method according to any one of claims 1 to 3, wherein an excess of solid  $CO_2$  is maintained in or upon the electrolyte throughout the entire coating operation.

6. A method according to any one of the preceding claims, wherein the electrolyte is maintained at a temperature which is below 40° F. but above the freezing point of the electrolyte.

7. A method according to any one of the preceding claims, wherein the electrolyte is maintained at a temperature of approximately 30° F. during the entire coating operation.

8. A method according to any one of the preceding claims, wherein the electrolyte comprises an aqueous solution of sulphuric acid having a concentration of 5 to 70% sulphuric acid.

9. A method according to any one of the preceding claims, in which the electrolyte

is agitated in order to maintain substantially uniform temperature conditions throughout the body of the electrolyte.

10. A method of producing a hard  
5 abrasion-resistant oxide coating on the surface of a predominantly aluminum or aluminum alloy article, which method is substantially as described.

11. A predominantly aluminum article  
10 having on its surface an abrasion-resis-

tant oxide coating consisting principally of aluminum oxide, which coating is produced by the method according to any one of the preceding claims.

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